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DMIC review OF RECENT DEVELOPMENTS

Oxidation-Resistant Coatings for Refractory Metals

B. C. Allen • February 2, 1968

COATING-PROCESS DEVELOPMENT FOR COLUMBIUM AND TANTALUM ALLOYS

Solar has deposited coatings consisting of chromium-titanium-silicon on Cb-752 and D-43 columbium alloys from fused fluoride or chloride salt baths by mean of electrolytic and nonelectrolytic techniques.[1] Thermodynamic and kinetic considerations limited the order in which the individual elements could be applied, and chromium and titanium could not be codeposited. The order of deposition found most practical was chromium, silicon, and titanium. A subsequent diffusion treatment produced primarily $(Cr, Ti)_5 Si_3$. The resulting oxidation resistance afforded the substrate was about 7 to 15 1-hour cycles in 2000 to 2600 F temperature range. Premature failure occurred by eruptions within the coatings, but the cause was not positively indentified.

TRW is developing manufacturing methods for coating columbium and tantalum alloys.[2,3] In the former, a production-scale facility is being developed to apply chromium-titanium-silicon coating to large (26 x 26 x 40 inches) columbium-alloy parts. Both vacuum-pack and slurry-application methods will be utilized. In the other work, a process is being developed for application of W/Si-W duplex coating on tantalum alloys (12 x 12 x 18 inches). The tungsten barrier is applied by chemical vapor depositions, electrophoretic deposition, or slurry-sinter techniques. The silicide coating is formed by a vacuum-pack or vacuum-slip-pack process.

COATING DEVELOPMENT FOR COLUMBIUM AND TANTALUM ALLOYS

A variety of protective coatings for columbium alloys has been investigated by Solar.[4] Thermal expansion, interdiffusion, and oxidation resistance were determined on potentially ductile sublayer columbium alloys, MAl* and MAl_3 aluminides, and MSi_2 and M_5Si_3 silicides. Diffusion barriers between titanium-chromium modifier and substrate were also evaluated; molybdenum and tungsten were the most effective. Coating systems studied included V-(80Cr-20Ti)-Si, V-(Cr-Ti)-Al-Si, (95Mo-5Ti)-Si, and Mo-Cr-(Fe-25Cr-5Al), and were generally applied by pack cementation. The vanadium-containing systems were designed to reduce Laves phase formation and severity of the interstitual sink effect, while (95Mo-5Ti)-Si had expansion coefficients similar to those of the substrate. The metal coating was intended to enhance ductility by having an all body-centered-cubic sequence, but interdiffusion appeared to limit the system to 10 hours at 2300 F. The V-(80Cr-20Ti)-Si coating, the most extensively studied, exhibited a minimum oxidation life of about 100 1-hour cycles at 1600 and 2400 F on D-43, Cb-752, and Cb-132M columbium alloys. The addition of aluminum to the coating had little effect. On the basis of limited tests, the slurry-sinter coating of (95Mo-5Ti)-Si with 10 percent iron or glass impregnation appeared to give even greater oxidation protection. The V-(80Cr-20Ti)-Si/D-43 or Cb-752 systems were extensively evaluated for aerospace and gas-turbine applications, and included seven different oxidation tests as well as tensile, creep, bend, and fatigue tests. The coating process reduced tensile strength of 0.012- and 0.030-inch-thick sheet generally 20 to 30 percent at 77 and 2200 F, reduced 10^6-cycle fatigue strength 50 percent at 77 F, and , for Cb-752 only, caused embrittlement at 77 F. Fatigue strength was unchanged after expansion for 15 hours at 2400 F. Creep results indicate that the coating could withstand up to 5 percent elongation at 2200 and 2400 F.

* M stands for columbium, titanium, chromium, vanadium, molybdenum, tungsten, zirconium, hafnium, tantalum, or various combinations.

TRW is also developing aluminide and silicide coatings for protection of columbium alloys for hundreds of hours at 2500 F.[5] Benefical modifications are expected by additions of vanadium, molybdenum, chromium, and titanium. Deposition technique for vanadium and molybdenum are being developed.

In another program, TRW is developing coatings for tantalum alloys for use in oxidizing atmospheres at 2000 to 3500 F.[6] In a three-part program, the following coatings are being evaluated: (1) hafnium-tantalum, tungsten/iridium, tungsten/silicon, (2) 18 hafnium alloys leading to layered, metal-bonded oxide coatings, the outer layer of which is formed in situ during oxidation, and (3) metal-bonded refractory oxide over an intermediate diffusion-alloy layer. Since discouraging results were obtained in the first two phases, future efforts will be devoted to the third phase.

COATING DEVELOPMENT FOR TUNGSTEN

Complex oxides of different structure types are being evaluated by Battelle's Columbus Laboratories as candidates for protecting tungsten at 3500 F.[7] The oxides are $SrZrO_3$ (perovskite), $Nd_2Zr_2O_7$ (pyrochlore), and $Yb_2Zr_2O_7$ (fluorite). The vaporization, structural stability, and interaction with tungsten and oxygen are being investigated under vacuum, reducing, inert, and oxidizing environments.

PROPERTY STUDIES OF COATED COLUMBIUM AND TANTALUM ALLOYS

NASA Langley has investigated protection of Ta-10W alloy by the slurry Sn-23.5Al-Mo coating.(8) The coating provided protection for about 2 hours in static air at 2900 F. Flowing air (subsonic) reduced the lifetime by a factor of four. Addition of more molybdenum (7 compared with 5.5 percent) appeared to give some increase in life in flowing air. Use of 6-minute cycles reduced the lifetime by a factor of two in static air. The coating caused little change in substrate tensile strength and elastic modulus at temperatures up to 2900 F even after 5 hours' exposure at 2600 F. However, room-temperature elongation of 0.008-inch-thick sheet was reduced by about a factor of two, and 0.025-inch-thick sheet was somewhat less affected. Elongation was about 10 to 20 percent at 2000 to 2900 F, and about 5 percent at 1700 F. Prior exposure for 5 hours at 2600 F reduced the tensile elongations to 1 to 7 percent. Limited tests indicated that gradated intermetallic/oxide coatings ($MoSi_2$ or WSi_2/ stabilized ZrO_2) have good spalling resistance after cyclic oxidation.

The performance capabilities of fused-slurry, complex silicide coatings on columbium alloy sheet has been evaluated by Lockheed-California.(9) Sylcor R512E (20Cr-20Fe-60Si) protected Cb-752 alloy over 8 hours at 2600 F at 0.1 torr, and over 8 hours at 2800 F at 1 and 10 torr air pressure. The system survived twenty 2.2-hour cycles of temperature up to 2500 F and pressures of 0.01 to 1000 torr, which simulated reentry conditions. Temperature capabilities of similar systems Cb-752/R512A (20 Cr-5Ti-75Si), D-43/R512A, and D-43/R512E appeared to be about 100 F lower.

McDonnell-Douglas is also evaluating the system Cb-752/R512E under temperature (up to 2600 F) -pressure (10^{-4} to 25 torr)-stress(0-40,000 psi) -time profiles representative of hypersonic flight.(10) Particular attention will be given to joints, faying surfaces, defect sensitivity, and reuse capability of spacecraft hardware.

McDonnell-Douglas is developing self-sustaining, radiating, coated tantalum-alloy structures for operation to 3600 F.(11) Oxidation-resistance and room- and elevated-temperatue mechanical-property tests are being conducted on various system, including T-222 tantalum alloy and Solar (95W-5Ti)-Si and Sylcor W/WSi_2 coating systems. Fabricability tests are being conducted with the intention of eventual testing of full-scale leading-edge and flat-panel components.

Fundamental processes involved in the protection of columbium and tantalum by their silicides are being studied at the City College Research Foundation.(12) The program consists of four parts: (1) establishment of thermochemical data for silicides employing an entirely solid-state electrochemical cell, (2) protection of both coating and substrate by glasses formed during oxidation, (3) use of coating modifiers to promote the formation of glassy films, and (4) interactions between intermediate phases, coating, and substrate, and the use of diffusion barriers to retard growth of intermediate phases.

A portion of a recent University of Dayton Research Institute effort was concerned with evaluation of D-43/R512A silicide and Cb-752, WC-103, and WC-129/Vac-Hyd Lunite 2 aluminide.(13) The as-coated D-43 columbium alloy retained full bend ductility to -60 F and showed no evidence of room-temperature embrittlement after 30 hours in static air at 2600 F. The excellent throwing power of the silicide was evident by complete penetration of spot-welded lap joints. Lifetimes of 12 and 23 hours at 2600 F at 95 percent reliability were found for the 2.75- and 4.4-mil-thick coating, respectively. Somewhat better performance was noted at 2400 F. In contrast, the Lunite 2 and modified Lunite 2 (ND 66-1) coatings failed in less than 2 hours at 2600 F and survived about 2 to 5 hours at 2400 F.

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